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Original Paper

# The origin of Zn Isotope Fractionation in Sulfides

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**Abstract:**

Isotope fractionation of Zn between aqueous sulfide, chloride, and carbonate species ($Zn^{2+}$, $Zn(HS)_2$, $Zn(HS)_3^-$, $Zn(HS)_4^{2-}$, $ZnS(HS)^-$, $ZnCl^+$, $ZnCl_2$, $ZnHCO_3^+$, and $ZnCO_3$) was investigated using *ab initio* methods. Only little fractionation is found between the sulfide species, whereas carbonates are up to 1‰ heavier than the parent solution. At pH>3 and under atmospheric-like $CO_2$ pressures, isotope fractionation of Zn sulfides precipitated from sulfidic solutions is affected by aqueous sulfide species and the $\delta^{66}Zn$ of sulfides reflect these in the parent solutions. Under high $P_{CO_2}$ conditions, carbonate species become abundant. In high $P_{CO_2}$ conditions of hydrothermal solutions, Zn precipitated as sulfides is isotopically nearly unfractionated with respect to a low-pH parent fluid. In contrast, negative $\delta^{66}Zn$ down to at least –0.6‰ can be expected in sulfides precipitated from solutions with pH>9. Zinc isotopes in sulfides and rocks therefore represent a potential indicator of mid to high pH in ancient hydrothermal fluids.

**Keywords:** Zinc, ligand, ocean, quantum chemical calculation, isotope fractionation

## 1. INTRODUCTION

Measurements of isotopic variations of Zn with a precision routinely better than 50 ppm have been reported in natural samples (see Albarede, 2004; Cloquet, 2008 for reviews). Presently, the interpretation of these isotopic variations is limited by our knowledge of the fractionation involved during chemical reactions, especially for species relevant to the present and ancient oceans, such as Zn chloride and Zn sulfides. Isotope fractionations created in Zn(II)-Zn(II) ligand exchange reactions (Maréchal and Albarède, 2002; Fujii et al., 2010) and in Zn(II)-$Zn^0$ redox reactions (Kavner et al., 2008; Fujii et al., 2009a) have been experimentally observed. Preliminary estimates of Zn isotope fractionation were provided in abstract form by Schauble (2003), while extensive calculations using *ab initio* techniques allowed Zn isotope fractionation to be assessed for aquo-, chloro-, sulfato-, and other dissolved $Zn^{2+}$ species (Black et al., 2011).

The role of sulfides is central to a broad range of prevalent geological scenarios and in particular the status of sulfur in ancient oceans is an outstanding issue (Canfield, 1998). Thermodynamic calculations for Zn sulfides and hydrosulfides have been carried out with the aim of assessing the chemistry of Proterozoic and Archean oceans (Saito et al., 2003). Hydrothermal vent solutions discharging either at mid-ocean ridges (Edmond et al., 1979) or along subduction zones (Mottl et al., 2004) comprise another environment dominated by sulfides. The solubility of sphalerite (ZnS) and speciation in sulfide solutions have also been studied (Bourcier and Barnes, 1987; Hayashi et al., 1990; Daskalakis and Helz, 1993; Tagirov et al., 2007; Tagirov and Seward, 2010). Tagirov et al. (2007) determined the stoichiometry and stability of Zn sulfide/hydrosulfide complexes at 373 K and concluded that the major species are

64 $Zn(HS)_2^0$ , $Zn(HS)_3^-$, and $ZnS(HS)^-$. Their Zn speciation model was consistent with that
65 of Bourcier and Barnes (1987), but different from other models (Hayashi et al., 1990;
66 Daskalakis and Helz, 1993), and was further expanded and strengthened in recent work
67 (Tagirov and Seward, 2010). The present work takes on the task of evaluating Zn
68 speciation and isotope fractionation among the different Zn sulfide species present in
69 geological fluids between 298 and 573 K. It largely relies on the stability analysis of
70 Tagirov et al. (2010) and complements the recent work by Black et al. (2011) on Zn
71 isotope fractionation in solution.
72
73 **2. COMPUTATIONAL METHODS**
74 Orbital geometries and vibrational frequencies of aqueous Zn(II) species were computed
75 using density functional theory (DFT) as implemented by the Gaussian03 code (Frisch
76 et al., 2003). The DFT method employed here is a hybrid density functional consisting
77 of Becke's three-parameter non-local hybrid exchange potential (B3) (Becke, 1993)
78 with Lee-Yang and Parr (LYP) (Lee et al., 1988) non-local functionals. In a quantum
79 chemical study, the convergence of the reaction energies of Zn(II) species is excellent in
80 6-311+G(d,p) or higher basis sets (Rulíšek and Havlas, 1999). Hence, the 6-311+G(d,p)
81 basis set, which is an all-electron basis set, was chosen for H, C, O, S, and Zn. For the
82 solvation effect, the CPCM continuum solvation method (CPCM: conductor-like
83 polarizable continuum model) was used. The geometry optimization and intramolecular
84 vibrational frequency analysis were performed for the hydrated Zn ion, hydrated Zn
85 carbonates, and hydrated Zn sulfides. For hydrated Zn chlorides, the results were
86 reproduced from our previous study (Fujii et al., 2010).
87

## 3. RESULTS AND DISCUSSION

### 3.1 Basis for the isotope fractionation theory in systems at equilibrium

A chemical exchange reaction can be represented as two half-reactions,

$$AX + Y \rightleftarrows AY + X, \quad (1)$$

or

$$A'X + Y \rightleftarrows A'Y + X, \quad (2)$$

where A and A' are the heavy and light isotopes of the element A, and X and Y represent ligands. The difference between half-reactions 1 and 2 corresponds to an isotopic exchange reaction between AX and AY,

$$A'Y + AX \rightleftarrows A'X + AY, \quad (3)$$

The isotope separation factor $\alpha$ between AX and AY is defined as

$$\alpha = \frac{([A]/[A'])_Y}{([A]/[A'])_X} \quad (4)$$

where $([A]/[A'])_X$ and $([A]/[A'])_Y$ are the isotopic ratios of A/A' measured in the complexes AX (and A'X) and AY (and A'Y), respectively. The isotope enrichment factor is defined as $\alpha_m - 1$. Since $\alpha$ is close to 1, $\alpha - 1$ can be approximated as $\ln \alpha$.

105 Isotopic deviations in parts per 1000 are conventionally defined as

$$\delta = \left( \frac{([A]/[A'])_{species}}{([A]/[A'])_{reference}} - 1 \right) \times 1000 \quad (5)$$

106

107 If AX (and A'X) is the major component in the system, Σ[A]/Σ[A'] is approximated to
108 be $([A]/[A'])_X$ such that an approximation expression $\delta \approx 10^3 \ln \alpha$ works.

109 The standard theory of chemical isotope fractionation is based on
110 mass-dependent isotopic differences in vibrational energies of isotopologues (Urey,
111 1947; Bigeleisen and Mayer, 1947). The isotope enrichment factor is proportional to
112 $\left(\frac{1}{m'} - \frac{1}{m}\right)$ with $m$ and $m'$ the masses of two isotopes (prime represents the light
113 isotope). In a previous study on Zn isotope fractionation, we showed that the
114 contribution of other effects, such as the nuclear field shift effect (Bigeleisen, 1996;
115 Nomura et al., 1996; Fujii et al., 2009b) to ln α is <10% (Fujii et al., 2010). Therefore,
116 an adequate approximation of fractionation factors between different species may be
117 obtained by the conventional mass-dependent theory (Bigeleisen and Mayer, 1947). All
118 the calculations were made for the $^{66}Zn/^{64}Zn$ ratio which avoids odd even staggering
119 (King, 1984; Aufmuth et al., 1987; Fricke and Heilig, 2004; Fujii et al., 2009b).

120 The isotope enrichment (ln α) due to the intramolecular vibrations can be
121 evaluated from the reduced partition function ratio (RPFR) $(s/s')f$ (Bigeleisen and Mayer,
122 1947; Urey, 1947) defined as

123

$$\ln (s/s')f = \Sigma[\ln b(u_i') - \ln b(u_i)] \quad (6)$$

124 where

$$\ln b(u_i) = -\ln u_i + u_i/2 + \ln (1 - e^{-ui}) \quad (7)$$

125

126 In this equation, ν stands for vibrational frequency, *s* for the symmetry number of the
127 molecule, and $u_i = h\nu_i/kT$. The subscript *i* stands for the *i*th molecular vibrational level
128 with primed variables referring to the light isotopologue. The isotope enrichment factor
129 due to the molecular vibration can be evaluated from the frequencies summed over all
130 the different modes. The partition function ratio (*s*/*s*')*f* for isotopologues A'X and AX
131 (A'Y and AY, respectively) is noted $\beta_X$ ($\beta_Y$, respectively). In the isotopic exchange
132 reaction 3, isotope fractionation can be estimated from the relation $\ln \alpha \approx \ln \beta_Y - \ln \beta_X$.

133 In the present study, the optimized structures of hydrated $Zn^{2+}$ and hydrated Zn
134 sulfides were first analyzed for $^{64}Zn$. For each complex, intramolecular vibrational
135 frequencies ($\nu_i$) were analyzed. By substituting $\nu_i$ into Eq. (7), $\ln b(u_i')$ was determined.
136 Using the same molecular structures, $^{64}Zn$ was replaced by $^{66}Zn$ and the vibrational
137 frequency analysis was performed again to obtain $\ln b(u_i)$, from which ln β was then
138 determined.

139

140 **3.2. Assessment of *ab initio* calculations**

141 The isotope fractionation between hydrated $Zn^{2+}$ and aqueous Zn chlorides has been
142 investigated experimentally and theoretically at 294 K (Fujii et al., 2010). Calculations
143 carried out for $Zn(H_2O)_6^{2+}$, $Zn(H_2O)_{18}^{2+}$, $ZnCl(H_2O)_5^{+}$, $ZnCl_2(H_2O)_4$, $ZnCl_3(H_2O)_3^{-}$,
144 $ZnCl_3(H_2O)^{-}$, $ZnCl_4(H_2O)_2^{2-}$, and $ZnCl_4^{2-}$, allow for a comparison with the work of
145 Black et al. (2011). As intramolecular vibrational modes and their frequencies depend
146 on the cluster model and interatomic distances, the stability of each compound must
147 first be demonstrated. We first tested the effect of solvation of $Zn^{2+}$ ions by comparing

148 the small cluster $Zn(H_2O)_6^{2+}$, including only the first hydration shell (Fig. 1a and
149 electronic annex, Fig. S1) with the large cluster $Zn(H_2O)_{18}^{2+}$, in which the small cluster
150 is surrounded by 12 $H_2O$ molecules in a second hydration shell (see figure 1b of Li et al.,
151 1996). In the present study, the CPCM continuum solvation method was tested. For
152 $Zn(H_2O)_6^{2+}$, we used the dielectric constant of water $\varepsilon = 78.3553$. The results are shown
153 in Table 1 and were found to be consistent with those of Fig. 9 in Black et al. (2011)
154 (see electronic annex, Tables S1, S2, and S3). The presence of the second hydration
155 shell shortens the Zn-O bond distance by 0.014 Å in the first coordination shell.
156 Applying the CPCM method further shortens this distance by 0.012 Å. The CPCM
157 solvation method provides bond distances satisfactorily close to those obtained
158 experimentally (Dreier and Rabe, 1986; Matsubara and Waseda, 1989; Maeda et al.,
159 1995).

160 The calculated $\nu_1$ frequencies (totally symmetric vibration, see Fig. S1) of
161 $Zn(H_2O)_6^{2+}$ in this study and Fujii et al. (2010) are much smaller than the literature
162 values obtained experimentally (Table 1). With the second hydration shell present, the
163 calculated $\nu_1$ frequency of $Zn(H_2O)_{18}^{2+}$ agrees with the experimental value of 380 $cm^{-1}$
164 (Yamaguchi et al., 1989). This frequency was not reproduced very well when the
165 CPCM method was applied to a model including only the inner hydration shell.

166 Since the conventional Bigeleisen-Mayer equation (Bigeleisen and Mayer,
167 1947) involves vibrational frequencies, an accurate evaluation of $\nu_1$ is in order. Besides
168 $\nu_1$, other vibrational modes, *e.g.*, asymmetric modes of $\nu_3$ and so on (see Fig. S1), are
169 also important to evaluate RPFR (see Eqs. 6 and 7 and Black et al., 2011). The $\nu_2$ and $\nu_3$
170 frequencies are shown in Table 1. As for $\nu_1$, adding the second hydration shell increases
171 the $\nu_2$ and $\nu_3$ frequencies and brings them closer to experimental observations (Rudolph

and Pye, 1999; Mink et al., 2003). Addition of the second hydration shell is therefore more effective than resorting to the CPCM solvation method.

The ln β values at 273, 423, and 573K (25, 150, and 300°C, respectively) calculated by using Eqs. (6) and (7) are shown in Table 2. The accuracy in RPFRs estimated by *ab initio* method is discussed in Rustad et al. (2010). It is clear that applying the CPCM solvation method does not significantly affect the value of ln β, whereas adding a second hydration shell with 12 $H_2O$ molecules increases ln β by 0.3‰ at 298 K. A similar phenomenon was found in our previous study on $Pd^{2+}$ isotope fractionation (Fujii et al., in press).

### 3.3. β-factors of aqueous Zn sulfides

The structure of the Zn sulfides was calculated with small cluster models without additional shells. $Zn^{2+}$ and Zn hydrogensulfides are related through the following stepwise reactions,

$$Zn^{2+} + HS^- \rightleftarrows ZnSH^+ \quad (8)$$

$$ZnHS^+ + HS^- \rightleftarrows Zn(HS)_2 \quad (9)$$

$$Zn(HS)_2 + HS^- \rightleftarrows Zn(HS)_3^- \quad (10)$$

$$Zn(HS)_3^- + HS^- \rightleftarrows Zn(HS)_4^{2-} \quad (11)$$

190

191 *Calculations for $ZnSH^+$.*

192 The formation of Zn mono-hydrogensulfide has been suggested on the basis of
193 voltammetric data (Zhang and Millero, 1994), but was later questioned (Luther et al.,
194 1996). Reaction 8 was disregarded by studies on sphalerite (ZnS) solubility in sulfide
195 solutions (Bourcier and Barnes, 1987; Hayashi et al., 1990; Daskalakis and Helz, 1993;
196 Tagirov et al., 2007; Tagirov and Seward, 2010). Though we tested the structural
197 optimization of $ZnHS(H_2O)_5^+$, this model complex is unstable and deforms into
198 $ZnHS(H_2O)_4^+$ with the 5th water molecule moving out of the inner coordination shell,
199 which suggests that the stability constant of reaction 8 is very small. A
200 hydroxide-hydrogensulfide species, $Zn(OH)HS^+$, has been reported (Bourcier and
201 Barnes, 1987; Hayashi et al., 1990), but its existence was not confirmed (Tagirov et al.,
202 2007; Tagirov and Seward, 2010).

203

204 *Calculations for $Zn(HS)_2$.*

205 In a theoretical study on Zn sulfides (Tossell and Vaughan, 1993), a tetrahedral
206 structure $Zn(HS)_2(H_2O)_2$ has been reported as $Zn(HS)_2$. The structure of
207 bis-hydrogensulfide for six-coordination transition metals is considered to be similar to
208 that of *trans*-$Mn(HS)_2(H_2O)_4$ (Rickard and Luther, 2006). We calculated the optimized
209 structure for the recommended structure $Zn(HS)_2(H_2O)_4$ (Fig. 1b) and the bond lengths
210 are shown in Table 1. The ln β value at 298 K is 2.72‰.

211

*Calculations for $Zn(HS)_3^-$.*

The calculations for the 6-coordinated $Zn(HS)_3(H_2O)_3^-$ did not converge. $HS^-$ forms stronger bonds with $Zn^{2+}$ than $H_2O$, and 3 $HS^-$ molecules tend to form a triangle, with $Zn^{2+}$ at the center (see figure 1 of Tossell and Vaughan, 1993). Tossell and Vaughan (1993) reported that $Zn(HS)_3^-$ and $Zn(HS)_3(OH)^{2-}$ are the most stable of the tri-hydrogensulfide species. The hydrolyzed species $Zn(HS)_3(OH)^{2-}$ has been considered in earlier solubility studies of sphalerites (Hayashi et al., 1990; Daskalakis et al., 1993), but its existence was later dismissed (Tagirov et al., 2007; Tagirov and Seward, 2010).

The existence of a species $Zn(HS)_3^-$ lacking direct Zn-water coordination is unlikely in aqueous solution. Tossell and Vaughan (1993) reported the presence of the mono-hydrated tri-hydrogensulfide species, $Zn(HS)_3H_2O^-$, and our calculations reproduced this structure (see figure 1 of Tossell and Vaughan, 1993). $Zn(HS)_3$ keeps the triangular plane with one $H_2O$ molecule bound to the plane via a hydration bond ($H_2O$-$Zn^{2+}$) and $OH_2$-SH hydrogen bonds. The hydrogen bond appears stronger than the hydration bond, which suggests that an extra $H_2O$ molecule may bind to the opposite side of the $Zn(HS)_3$ plane to form $Zn(HS)_3(H_2O)_2^-$. The structure after convergence is shown in Fig. 1c. However, even though the plane symmetric arrangement with two $H_2O$ molecules with respect to the $Zn(HS)_3$ plane is possible, the Gibbs free energy was 1.09 kJ/mol larger and this model complex is therefore not chosen.

The bond distances are shown in Table 3. The longer Zn-O bond distance suggests that the $H_2O$ molecules possibly are bound to $Zn(HS)_3$ via the hydrogen bonds of $OH_2$-SH. The ln β value at 298 K is 3.03‰ (Table 2).

235

236 *Calculations for $Zn(HS)_4^{2-}$.*

237 Solubility measurements of sphalerites in sulfide solutions (Bourcier and Barnes, 1987;
238 Hayashi et al., 1990; Daskalakis and Helz, 1993) considered the presence of a
239 tetra-hydrogensulfide species $Zn(HS)_4^{2-}$; its mole fraction is expected to decrease with
240 temperature (Tagirov and Seward, 2010). A possible tetrahedral structure (Fig. 1d) was
241 suggested by Tossell and Vaughan (1993). The tetrahedral structure of $Zn(HS)_4^{2-}$ is
242 similar to a unit cell of Zn sulfide clusters (Luther et al., 1999; Luther and Rickard,
243 2005). Our results are shown in Tables 2 and 3. The ln β value at 298 K shows the
244 smallest value (2.19‰, Table 2) of all Zn sulfides.

245

246 *Calculations for $ZnS(HS)^-$.*

247 A distinctive feature in the solubility trend of sphalerite calculated by Tagirov et al.
248 (2007) and Tagirov and Seward (2010) is that $ZnS(HS)^-$ appears to be a prevalent
249 sulfide species at pH>10 and temperatures <473 K. With increasing pH, complexation
250 proceeds from $Zn(HS)_3^-$ to $Zn(HS)_4^{2-}$ and $ZnS(HS)^-$ (Tagirov and Seward, 2010).
251 Formation of $ZnS(HS)^-$ from $Zn(HS)_4^{2-}$ with increasing pH results from the reaction

252

$$Zn(HS)_4^{2-} + OH^- \rightleftarrows ZnS(HS)(H_2O)^- + 2HS^- \quad (12)$$

253

254 A few *ab initio* calculation studies on anhydrous Zn sulfides (Cini, 1999) or clusters of
255 Zn sulfides (Luther et al., 1999; Luther and Rickard, 2005) have been reported. To the
256 best of our knowledge, structural data of monomeric $ZnS(HS)^-$ in aqueous solutions are

not available. Spatially, water molecules may interact with Zn(II) in $ZnS(HS)^-$ as $ZnS(HS)(H_2O)_n^-$. The coordination number of Zn(II) in the monomeric species $ZnS(HS)(H_2O)^-$ is three, but this coordination number is too small if this species exists in aqueous solution. Since the aggregation of complexes increases the coordination probability, $ZnS(HS)(H_2O)^-$ is considered to be a simplified formula of polymerized species $n[ZnS(HS)(H_2O)^-]$. Let us consider a dimer for $n = 2$.

Stereochemically, dimerization of $ZnS(HS)^-$ from $Zn(HS)_3(H_2O)_3^-$ may be natural (see Fig. 1c and 1e).

$$2Zn(HS)_3(H_2O)_2^- + 2OH^- \rightleftarrows Zn_2S_2(HS)_2(H_2O)_2^{2-} + 2SH^- + 4H_2O \quad (13)$$

where $Zn_2S_2(HS)_2(H_2O)_2^{2-}$ can be expressed as $2[ZnS(HS)H_2O^-]$. Zn(II) has a coordination number of 5 in this species. Since $S^{2-}$ has the tetrahedral coordination property, two $S^{2-}$ ions bridging to two $Zn^{2+}$ ions may also bind to $H_2O$ in the outer sphere. More $H_2O$ molecules may be arranged on the triangular $Zn(HS)_3$ plane. $ZnS(HS)(H_2O)_n^-$ with $n \geq 2$ may exist.

$Zn(HS)_3^-$ and $ZnS(HS)^-$ possess the trigonal planar of $ZnS_3$ core, while $Zn(HS)_4^{2-}$ is tetrahedral. Large entropic changes via structural changes in the reaction $Zn(HS)_3^- \leftrightarrow Zn(HS)_4^{2-} \leftrightarrow ZnS(HS)^-$ are expected due to the existence of intermediate state $Zn(HS)_4^{2-}$. With the increase of temperature, the mole fraction of $Zn(HS)_4^{2-}$ drastically decreases (Tagirov and Seward, 2010). This suggests a direct reaction pathway between $Zn(HS)_3^-$ and $ZnS(HS)^-$ at high temperatures. This reaction path of

reaction 13 would be entropically favorable. The bond distances of 2[ZnS(HS)$H_2O^-$] are shown in Table 3. The ln β value at 298 K is 2.63‰ (Table 2).

*Calculations for Zn carbonates.*

In the present work, we calculated the ln β values for Zn isotope fractionation (Table 2) for hydrated Zn carbonates, $ZnHCO_3(H_2O)_4$, and $ZnCO_3(H_2O)_4$, in which $HCO_3^-$ and $CO_3^{2-}$ are treated as bidentate ligands (see Figs. 1f and 1g) using the same techniques as Fujii et al. (2011) for Ni. Zinc is isotopically heavy in carbonates relative to hydrated $Zn^{2+}$ and Zn sulfide species. The ln β values are larger than those of $Zn(H_2O)_6^{2+}$, Zn sulfides, and Zn chlorides. They compare with the ln β values reported by Black et al. (2011) on Zn sulfates. Upon reduction of sulfates to sulfides in the presence of carbonate ions, a strong fractionation of Zn isotopes may be expected in the sulfide-carbonate system.

### 3.4. Zn isotope systematics between aqueous sulfides and chlorides

Isotope fractionation relevant to $Zn(H_2O)_6^{2+}$, $Zn(HS)_2(H_2O)_4$, $Zn(HS)_3(H_2O)_2^-$, $Zn(HS)_4^{2-}$, 2[ZnS(HS)$H_2O^-$], $ZnCl(H_2O)_5^+$, $ZnCl_2(H_2O)_4$, $ZnHCO_3(H_2O)_4^+$, and $ZnCO_3(H_2O)_4$ will now be evaluated. The structure and ln β of Zn chlorides were reproduced from our previous study (Fujii et al., 2010) with calculations extended to higher temperatures. The temperature dependence of ln β can be estimated from the values compiled in Table 2. The total range of variation of ln β at 298 K is ~2‰. We calculated the speciation and isotopic fractionation of Zn for a total concentration of sulfur Σ[S] of 0.1 M in the absence of $Cl^-$ ([$Cl^-$] = 0 M) and carbonates (Σ[C] = 0 M) at

298, 423, and 573 K as a function of pH. In our calculation, free $Cl^-$ concentration is just treated as a parameter without considering association/dissociation reactions of HCl and chlorides at various temperatures. In principle, activities should be used throughout rather than concentrations, but the precise compositions of hydrothermal solutions are rarely known, and uncertainties on isotope fractionation attached to the non-ideal character of electrolyte solutions are certainly negligible with respect to those resulting from the poorly constrained chemistry of hydrothermal systems. As a result, the activity coefficients were considered equal to unity. As a dilute system, molar concentrations are used instead of molal concentrations. All calculations were performed under an assumption that the molecular structures remain the same by increasing temperature.

The following chemical equilibrium reactions were investigated,

$$Zn^{2+} + 2HS^- \rightleftarrows Zn(HS)_2, \quad K_{Zn(HS)_2} \tag{14}$$

$$Zn^{2+} + 3HS^- \rightleftarrows Zn(HS)_3^-, \quad K_{Zn(HS)_3^-} \tag{15}$$

$$Zn^{2+} + 4HS^- \rightleftarrows Zn(HS)_4^{2-}, \quad K_{Zn(HS)_4^{2-}} \tag{16}$$

$$Zn^{2+} + 2HS^- \rightleftarrows ZnS(HS)^- + H^+, \quad K_{ZnS(HS)^-} \tag{17}$$

317 It should be noted that, in the present study, we use *K* for cumulative formation constant
318 β in order to avoid confusion about ln β of isotope fractionation.
319 Under reducing conditions with negligible sulfate formation, the total concentration of
320 sulfur (Σ[S] = 0.1 M) is controlled by the following dissociation reaction,
321

$$H_2S \rightleftarrows HS^- + H^+ \tag{18}$$

322
323 where we used the relation,

$$\log \frac{[HS^-]}{[H_2S]} = -pK_a + pH \tag{19}$$

324
325 The stability constants and acid dissociation constants ($pK_a$) at 298, 423, and 573 K
326 used are listed in Table 4. Since $pK_a$ was determined under the existence of $Na^+$, strictly,
327 it includes an effect of NaHS dissociation.
328 We also calculated the speciation and isotopic fractionation of Zn isotologues
329 under typical hydrothermal conditions, with Σ[S] = 5 mM (Von Damm, 1990) and [$Cl^-$]
330 = 0.55 M (Macleod et al., 1994) at 298, 423, and 573 K and for variable pH. We set
331 $P_{CO_2}$ at 50 bar (log $P_{CO_2}$ = 1.6), which corresponds to a water (total) pressure of $10^5$
332 Pa (1 kbar) and a mole fraction of $CO_2$ of 5 percent (Rose et al., 1996). Such values
333 conveniently describe the conditions at about 3 km below the sea floor. The following
334 chemical equilibrium reactions also were investigated,
335

$$Zn^{2+} + Cl^{-} \rightleftarrows ZnCl^{+}, \quad K_{ZnCl^{+}} \tag{20}$$

336

$$Zn^{2+} + 2Cl^{-} \rightleftarrows ZnCl_2, \quad K_{ZnCl_2} \tag{21}$$

337

$$Zn^{2+} + HCO_3^{-} \rightleftarrows ZnHCO_3^{+}, \quad K_{ZnHCO_3^{+}} \tag{22}$$

338

$$Zn^{2+} + CO_3^{2-} \rightleftarrows ZnCO_3, \quad K_{ZnCO_3} \tag{23}$$

339

340 For carbonates, the following gas-liquid equilibrium reactions were considered.

341

$$CO_2 + H_2O \rightleftarrows HCO_3^{-} + H^{+}, \quad K_{HCO_3^{-}} \tag{24}$$

342

$$CO_2 + H_2O \rightleftarrows CO_3^{2-} + 2H^{+}, \quad K_{CO_3^{2-}} \tag{25}$$

343

344 The ionization of carbonic acid at elevated temperatures has been studied by Read
345 (1975) and Patterson et al. (1982, 1984). The acid dissociation constant between the
346 hydrogen carbonate ion ($HCO_3^{-}$) and the carbonate ion ($CO_3^{2-}$) is the ratio of $K_{HCO_3^{-}}$
347 and $K_{CO_3^{2-}}$. These values at 298, 423, and 573 K (Smith et al., 1986), in which the
348 original data are taken from (Patterson et al., 1982; 1984), are shown in Table 4.

Because of the broad relevance of carbon dioxide to geological environments, we first investigated the effect of $P_{CO_2}$ on Zn isotope variability of Zn in sulfidic hydrothermal environments. As a reference, speciation and isotope fractionation are first investigated for hydrothermal solutions placed under the low $P_{CO_2}$ typical of equilibration with the modern atmosphere. Then, the discussion is extended to conditions of high $P_{CO_2}$ in order to constrain Zn isotope fractionation in solutions equilibrated with a high-$P_{CO_2}$ atmosphere or circulating in deep-seated hydrothermal systems.

The results are shown in Figs. 3, 4, and 5. Figs 3a, 4a, and 5a show quite good agreement with the reported mole fractions of aqueous Zn sulfide species estimated from stability constants of reactions 14-17 and solubility products of ZnS(crystal) (Tagirov and Seward, 2010). In the present study, $K_{ZnHCO_3^+}$ and $K_{ZnCO_3}$ at the standard temperature 298 K (Zirino and Yamamoto, 1972) were used for 423 and 573 K due to lack of reliable data of aqueous Zn carbonates at high temperature. Even if a tenfold larger $K_{ZnHCO_3^+}$ were used for 573 K (Fig 5b), the mole fraction of $ZnHCO_3^+$ would not visibly increase. Variations of $K_{ZnCO_3}$ mainly changes the mole fractions of $ZnCO_3$ and $ZnS(HS)^-$ but have little effect on the concentrations of other species. Increasing log $K_{ZnCO_3}$ by one unit increases the mole fraction of $ZnCO_3$ and decreases that of $ZnS(HS)^-$ by ~25% (see electronic annex, Fig. S2).

Isotope fractionation of Zn observed as $\delta^{66}Zn$ was estimated as shown in Figs. 3c, 3d, 4c, 4d, 5c, and 5d. The $\delta^{66}Zn$ value was calculated as follows. The bulk $^{66}Zn/^{64}Zn$ ratio is

371

$$\frac{\Sigma[^{66}Zn]}{\Sigma[^{64}Zn]} = \frac{[^{66}Zn^{2+}] + [^{66}Zn(HS)_2] + [^{66}Zn(HS)_3^-] + [^{66}Zn(HS)_4^{2-}] + [^{66}ZnS(HS)^-] + [^{66}ZnCl^+] + [^{66}ZnCl_2] + [^{66}ZnHCO_3^+] + [^{66}ZnCO_3]}{[^{64}Zn^{2+}] + [^{64}Zn(HS)_2] + [^{64}Zn(HS)_3^-] + [^{64}Zn(HS)_4^{2-}] + [^{64}ZnS(HS)^-] + [^{64}ZnCl^+] + [^{64}ZnCl_2] + [^{64}ZnHCO_3^+] + [^{64}ZnCO_3]} \quad (26)$$

372

373 Stability constants were calculated from ln β values. For example,

374

$$\ln \frac{K_{Zn(HS)_2}(^{66}Zn)}{K_{Zn(HS)_2}(^{64}Zn)} = \ln \frac{[^{66}Zn(HS)_2]/[^{64}Zn(HS)_2]}{[^{66}Zn^{2+}]/[^{64}Zn^{2+}]}$$

375

$$= \ln \beta_{Zn(HS)_2} - \ln \beta_{Zn^{2+}} \quad (27)$$

376

377 The value $\Sigma[Zn] = 10^{-6.1}$ M (Tagirov and Seward, 2010) was used, but is
378 inconsequential for the speciation calculation. The effect of ionic strength was neglected
379 and activity coefficients of all species were set to be unity in a diluted system, which
380 would be of no practical importance for isotope ratios.

381

382 **3.5 Zn isotope variability in solutions at low to intermediate temperatures**

383 *Low $P_{CO_2}$ conditions.*

384 Isotope fractionation between natural fluids and precipitates occurs when Zn distributes
385 itself between sphalerite, the prevalent Zn ore, and the parent fluid. Figures 3-5 indicate
386 that, as expected from the order of ln β (Figure 2), the various aqueous Zn sulfide
387 complexes are all isotopically lighter than $Zn^{2+}$ and Zn chlorides. Zinc isotope
388 fractionation in sulfide-rich solutions is controlled by the respective mole fractions of
389 hydrated $Zn^{2+}$ and aqueous sulfides and therefore is predicted to be pH-dependent. At

390 pH<3, Zn is largely present as $Zn^{2+}$ in fresh water and as Zn chlorides at seawater
391 chlorinities. High chlorine contents change the charge balance and therefore shift the
392 dependence of speciation with pH, but, overall, affect isotope fractionation patterns only
393 slightly (see electronic, Figs. S3, S4, and S5). Under conditions typical of equilibration
394 with the atmosphere, carbonate complexes can safely be neglected (Zirino and
395 Yamamoto, 1972). Sulfides precipitating from hydrothermal solutions should be
396 isotopically lighter than the solution, but the extent of isotope fractionation decreases
397 with temperature. Zn isotope fractionation between the plausible precursor species of
398 sphalerite, $Zn(HS)_2$ at low pH and $Zn(HS)_4^{2-}$ and/or $ZnS(HS)^-$ at high pH, is very small.
399 At pH>3, the dominant Zn species are aqueous sulfides (Tagirov and Seward, 2010).
400 Under the assumption that the isotopic composition of sphalerite is inherited from the
401 precursor species, little isotope fractionation between sphalerite and the fluid is
402 therefore expected (< 0.25‰) at 423 K and even less at higher temperatures.

403 In sulfide-free oxic seawater and fresh water equilibrated with the atmosphere,
404 metallic ion, chloride, hydroxide, and carbonate complexes dominate zinc speciation,
405 while Zn sulfate is a minor species (Zirino and Yamamoto, 1972; Turner et al., 1981;
406 Stanley and Byrne, 1990; Black et al., 2011). Zn in marine carbonates is about 1‰
407 heavier (Pichat et al., 2003) than seawater ($\delta^{66}$Zn~0‰) (Bermin et al., 2006), which is
408 consistent with Zn isotope fractionation observed at ~298 K between aqueous carbonate
409 species and the metallic ion or its chloride (see electronic annex, Fig. S6). Zn-O bonds,
410 as in zincite (ZnO) (Schauble et al. 2003), zinc sulfates (Black et al., 2011), and
411 presumably other oxo-anions tend to concentrate heavy Zn. An enrichment of Zn heavy
412 isotopes is therefore expected for zinc carbonates. Here we further assume that Zn

413 isotope fractionation between solid carbonates and the dissolved species $ZnCO_3$ can be
414 neglected.

415 *High $P_{CO_2}$ conditions.*

416 Carbonate, which is usually a minor species in surface waters, becomes a major player
417 in hydrothermal solutions when $P_{CO_2}$ rises at depth. Figs. 3b, 3d, 4b, 4d, 5b, and 5d
418 show that the presence of carbonate ions brings about a stark contrast between regions
419 of low pH (<8) and high pH (>9). We will restrict the discussion to sphalerite
420 precipitation when smithsonite ($ZnCO_3$) does not reach saturation. At low pH (pH <
421 $\mathrm{p}K_{HCO_3^-}$), the abundance of the aqueous $ZnCO_3$ species is very low and sphalerite
422 precipitates with nearly the same $\delta^{66}Zn$ as the original fluid, *i.e.*, with very little
423 fractionation. In contrast, at pH>9, most Zn is in aqueous carbonate form. ZnS is
424 considered to be formed from major sulfides $ZnS(HS)^-$ and/or $Zn(HS)_4^{2-}$ via
425 polymerization and dehydration. If isotope fractionation upon precipitation can be
426 neglected, the values of $\delta^{66}Zn$ for $ZnS(HS)^-$ and $Zn(HS)_4^{2-}$ are representative of those
427 eventually found in ZnS. Sphalerite is therefore expected to possess negative $\delta^{66}Zn$
428 values. Zinc is isotopically more negative in sphalerite with respect to the fluid, by
429 ~1.5‰ at 298 K, ~0.8‰ at 423 K, and ~0.4‰ at 573 K (see $\delta^{66}Zn$ of $ZnS(HS)^-$ and/or
430 $Zn(HS)_4^{2-}$ at pH >9). Strongly negative $\delta^{66}Zn$ in sphalerite therefore represents a
431 potential indicator of high pH in low- to high-temperature hydrothermal fluids.

432 The narrow range of Zn isotope fractionation, mostly 0.0 to 0.6‰ in natural
433 sphalerite from continental environments (Albarede, 2004; Kelley et al., 2009) and in
434 most serpentines (Pons et al., 2010), together with the lack of strong isotope

435 fractionation between ZnS and hydrothermal vent fluid from mid-ocean ridges at
436 temperatures >523 K (John et al., 2008) can be explained by the predominance of
437 chloride complexes and aquated $Zn^{2+}$ ion in solutions at pH<7. These observations
438 concur with limited computational evidence that sphalerite is not fractionated with
439 respect to tetrahedral $[ZnCl_4]^{2-}$ (Schauble et al., 2003). Sphalerite precipitation therefore
440 seems to take place by disproportionation of an aqueous sulfide species, most likely
441 $Zn(HS)_2(H_2O)_4$ and $ZnS(HS)H_2O^-$. Occasionally high $\delta^{66}Zn$ in hydrothermal fluids
442 (John et al., 2008) may reflect the prevalence of Zn leached out of carbonate and
443 FeMn-hydroxides ($\delta^{66}Zn$ >0.6 ‰) (Maréchal et al., 2000; Pichat et al., 2003) and not
444 from a basaltic source ($\delta^{66}Zn$ ~0.3 ‰).

445 In contrast, the negative $\delta^{66}Zn$ observed by Pons et al. (2010) in the mud
446 serpentine volcanoes of the Mariana associated with high-pH (10-12) interstitial fluids
447 (down to –0.2‰) (Mottl et al. 2004; Hulme et al., 2010), and by Mason et al. (2005) in
448 island arc-type base-metal deposits from the Urals (down to –0.4 ‰) carry the signature
449 of fractionation by sulfides in island arc hydrothermal solutions dominated by sulfate
450 and carbonates. Zinc-sulfate complexes are weak and much less abundant than chloride
451 and hydroxide complexes, even with the rather high sulfate contents typical of seawater
452 (Stanley and Byrne, 1990; Mottl et al. 2004; Black et al., 2011). The negative $\delta^{66}Zn$
453 values of sulfides precipitated from hydrothermal fluids therefore signal the stability of
454 Zn carbonates and hence pH in excess of the second p$K_a$ of carbonic acid. Zinc isotope
455 compositions in sulfides and rocks are potentially helpful in distinguishing low-pH from
456 high-pH hydrothermal solution.
457

458 **CONCLUSIONS**

459 Isotope fractionation of Zn in aqueous sulfidic solutions was found to be controlled by
460 aqueous zinc sulfide species, and for high $P_{CO_2}$ conditions, by zinc carbonate species.
461 In solutions equilibrated with the atmosphere, Zn is isotopically unfractionated in
462 sulfides and isotopically heavy in carbonates. Under the high $P_{CO_2}$ conditions of
463 hydrothermal solutions, Zn precipitated as sulfides is isotopically nearly unfractionated
464 with respect to a low-pH parent fluid. Negative $\delta^{66}$Zn down to 0.6‰ can be expected in
465 sulfides precipitated from solutions with high $P_{CO_2}$ and a pH > 9. Zn isotopes in
466 sulfides and rocks therefore represent a potential indicator of mid to high pH in ancient
467 hydrothermal fluids.

468

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474

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670 Table 1 Zn-O bond distances and $\nu_1$ frequencies determined for hydrated $Zn^{2+}$.

| Species | Method[a] | Zn-O (Å) | $\nu_1$ ($cm^{-1}$) | $\nu_2$ ($cm^{-1}$) | $\nu_3$ ($cm^{-1}$) | Reference |
|---|---|---|---|---|---|---|
| $Zn(H_2O)_6^{2+}$ | DFT | 2.128 | 333 | - | - | Fujii et al. (2010) |
| $Zn(H_2O)_6^{2+}$ | DFT[b] | 2.128 | 333 | 219 | 294 | This study |
| $Zn(H_2O)_6^{2+}$ | DFT[c] | 2.102 | 353 | 227 | 317 | This study |
| $Zn(H_2O)_{18}^{2+}$ | DFT[d] | 2.114 | 380 | - | - | Fujii et al. (2010) |
| $Zn(H_2O)_{18}^{2+}$ | DFT[d] | 2.114 | 380 | 298 | 362 | This study |
| - | XRD | 2.08 | - | - | - | Tossel (1991) |
| - | XRD | 2.15 | - | - | - | Maeda et al. (1995) |
| - | AXN | 2.10-2.15 | - | - | - | Matsubara and Waseda (1989) |
| - | EXAFS | 2.05-2.07 | - | - | - | Dreier and Rabe (1986) |
| - | Raman | - | 390±10 | - | - | Irish et al. (1963) |
| - | Raman | - | 379±5 | - | - | Yamaguchi et al. (1989) |
| - | Raman | - | 385 | - | - | Maeda et al. (1995) |
| - | Raman, IR | - | 390±2 | 270±5 | 365±5 | Rudolph and Pye (1999) |
| - | Raman, IR | - | 389 | 360 | 386 | Mink et al. (2003) |

671 [a] DFT (density functional theory), XRD (x-ray diffraction), AXN (anomalous x-ray scattering),
672 EXAFS (extended x-ray absorption fine structure), IR (infrared).
673 [b] DFT calculation results with various basis sets are given in electronic annex, Tables S1 and
674 S2.
675 [c] CPCM continuum solvation method was applied.
676 [d] 12 $H_2O$ molecules were arranged around $Zn(H_2O)_6^{2+}$.

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683 Table 2 Logarithm of the reduced partition function, ln β, for isotope pair $^{66}Zn/^{64}Zn$.

| Species | ln β at 298K (‰) | ln β at 423K (‰) | ln β at 573K (‰) |
|---|---|---|---|
| $Zn(H_2O)_6^{2+}$ [a] | 3.263<br>3.280[b] | 1.659<br>1.660[b] | 0.915<br>0.913[b] |
| $Zn(H_2O)_{18}^{2+}$ [a] | 3.576 | 1.819 | 1.004 |
| $Zn(HS)_2(H_2O)_4$ | 2.717 | 1.384 | 0.764 |
| $Zn(HS)_3(H_2O)_2^-$ | 3.028 | 1.535 | 0.845 |
| $Zn(HS)_4^{2-}$ | 2.190 | 1.101 | 0.604 |
| $ZnS(HS)H_2O^-$ | 2.628 | 1.326 | 0.728 |
| $ZnCl\ (H_2O)_5^+$ [a] | 3.142 | 1.599 | 0.882 |
| $ZnCl_2(H_2O)_4$ [a] | 2.956 | 1.495 | 0.822 |
| $ZnHCO_3(H_2O)_4^+$ | 3.439 | 1.754 | 0.969 |
| $ZnCO_3(H_2O)_4$ | 3.990 | 2.050 | 1.137 |

684 [a] Calculated structures (Fujii et al., 2010) were reproduced.
685 [b]Applying the CPCM continuum solvation method.
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699 Table 3 Bond distances calculated for Zn sulfides.

| Species | Bond[a], Zn-O (Å) | Bond[a], Zn-S (Å) |
|---|---|---|
| $Zn(HS)_2(H_2O)_4$ | 2.434(2)<br>2.514(2) | 2.295(2) |
| $Zn(HS)_3(H_2O)_2$ | 3.536(2) | 2.300(2)<br>2.324(1) |
| $Zn(HS)_4$ | – | 2.450(4) |
| $ZnS(HS)H_2O^-$ | 3.412(2)[b] | 2.331(2)[b]<br>2.365(1) |

700 [a] Numbers of bonds are shown in parentheses.
701 [b] Shared with another $Zn^{2+}$.
702

Table 4 Stability constants of Zn sulfide and chloride systems.

| | 298K | 423K | 573K | Reference |
|---|---|---|---|---|
| log $K_{Zn(HS)_2}$ | 9.40 | 9.82 | 12.56[a] | Tagirov and Seward (2010) |
| log $K_{Zn(HS)_3^-}$ | 13.06[a] | 12.39[b] | 14.41[a] | Tagirov and Seward (2010) |
| log $K_{Zn(HS)_4^{2-}}$ | 14.47 | 12.02[a] | 11.80[a] | Tagirov and Seward (2010) |
| log $K_{ZnS(HS)^-}$ | 3.41 | 2.69 | 2.47[a] | Tagirov and Seward (2010) |
| log $K_{ZnCl^+}$ | –0.03[c] | 2.89 | 6.53[c] | Ruaya and Seward (1986) |
| log $K_{ZnCl_2}$ | 0.13[c] | 2.96 | 7.51[c] | Ruaya and Seward (1986) |
| log $K_{ZnHCO_3^+}$ | 2.1 | 2.1[d] | 2.1[d] | Zirino and Yamamoto (1972) |
| log $K_{ZnCO_3}$ | 5.3 | 5.3[d] | 5.3[d] | Zirino and Yamamoto (1972) |
| log $K_{HCO_3^-}$ | –6.35 | –6.74 | –8.50 | Smith et al. (1986) |
| log $K_{CO_3^{2-}}$ | –16.69 | –16.98 | –19.82 | Smith et al. (1986) |
| p$K_a$ | 6.99 | 6.49 | 7.89 | Suleimenov and Seward (1997) |

[c] Values are shown in Appendix C in Tagirov and Seward (2010).
[b] Value for 373K was used. The value for 423K did not reproduce the speciation calculation of Tagirov and Seward (2010).
[c] Calculated from equation 23 in Ruaya and Seward (1986).
[d] Stability constants at 298 K.

726 **Figure captions**

727 **Figure 1 Molecular structures of hydrated $Zn^{2+}$ and aqueous Zn sulfides.** Structures
728 are drawn by using GaussView3.0 (Gaussian Inc.). a) $Zn(H_2O)_6^{2+}$, b) $Zn(HS)_2(H_2O)_4$, c)
729 $Zn(HS)_3(H_2O)_2^-$, d) $Zn(HS)_4^{2-}$, e) $Zn_2S_2(HS)_2(H_2O)_2^{2-}$ = $2[ZnS(HS)(H_2O)^-]$, f)
730 $ZnHCO_3(H_2O)_4^+$, and g) $ZnCO_3(H_2O)_4$.

731 **Figure 2 Temperature dependence of ln β.** The ln β values shown in Table 2 are fitted
732 by linear functions of $T^{-2}$.

733 **Figure 3 Mole fractions of Zn species and Zn isotopic variations as functions of pH**
734 **at 298 K.** a) Mole fractions of Zn species in $Cl^-$ and carbonate free hydrous fluid under
735 Σ[S]=0.1 M, b) Mole fractions of Zn species with Σ[S]=5 mM and $[Cl^-]$ = 0.55 M under
736 $P_{CO_2}$ = 50 bar, c) Species $\delta^{66}$Zn relative to the bulk solution in $Cl^-$ and carbonate free
737 hydrous fluid, and d) $\delta^{66}$Zn under the hydrothermal condition of b). Dotted lines at 0‰
738 in c) and d) show $\delta^{66}$Zn of bulk solution (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn]
739 was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

740 **Figure 4 Mole fractions of Zn species and Zn isotopic variations as functions of pH**
741 **at 423 K. Panels a-d : see caption of Fig. 3.** Mole fraction of $Zn^{2+}$ in Fig. 4b is 0.14%
742 at pH=2 and smaller than that at pH>2. The maximum value of $Zn(HS)_4^{2-}$ mole fraction
743 is 0.06% at pH=7.1 (Fig. 4b). Dotted lines in c) and d) mean $\delta^{66}$Zn of bulk solution
744 (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn] was set to be $10^{-6.1}$ M (Tagirov and
745 Seward, 2010).

746 **Figure 5 Mole fractions of Zn species and Zn isotopic variations as functions of pH**
747 **at 573 K. Panels a-d : see caption of Fig. 3.** Mole fraction of $Zn^{2+}$ in Fig. 5b is smaller
748 than 0.001%. The maximum value of $Zn(HS)_4^{2-}$ mole fraction is 0.02% (Fig. 5a) or

749 0.0002% (Fig. 5b) at pH=9.3. The maximum value of $ZnHCO_3^+$ mole fraction is 0.1%
750 at pH= 10.5 (Fig. 5b). Dotted lines in c) and d) mean $\delta^{66}Zn$ of bulk solution (averaged
751 $\delta^{66}Zn$ in the whole solution). $\Sigma$[Zn] was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).
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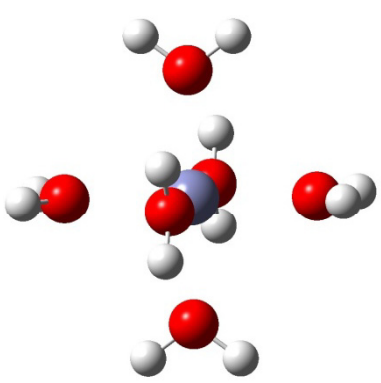
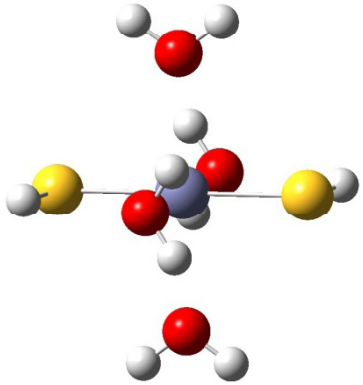
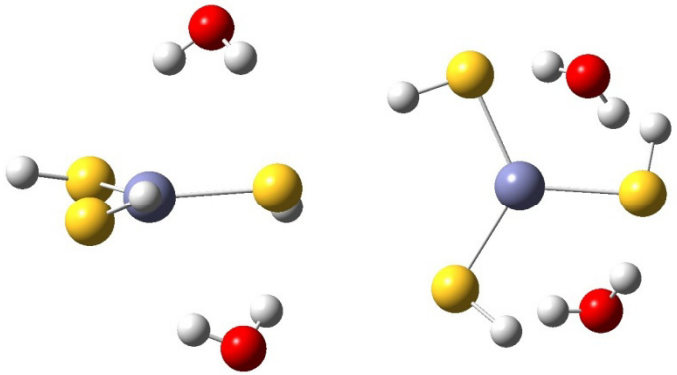


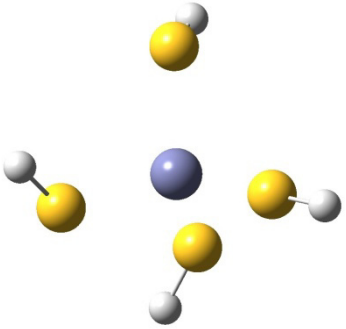
a) $Zn(H_2O)_6^{2+}$



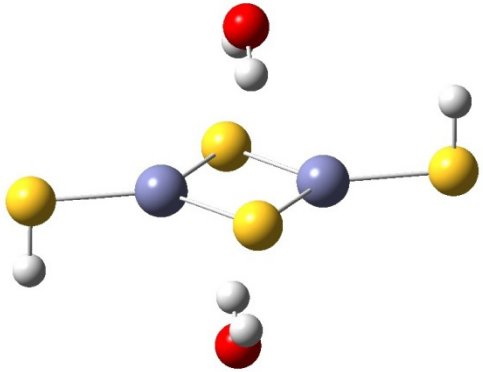
b) $Zn(HS)_2(H_2O)_4$



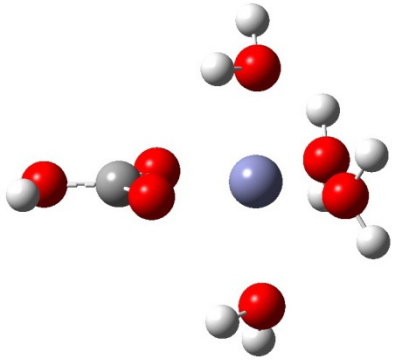
c) $Zn(HS)_3(H_2O)_2^-$ : side view (left), top view (right)



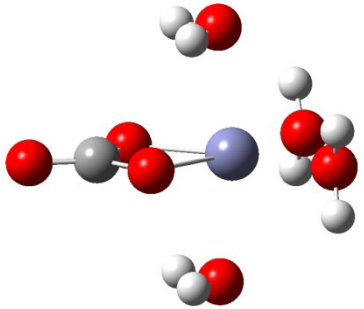
d) $Zn(HS)_4^{2-}$



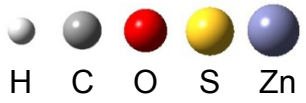
e) $Zn_2S_2(HS)_2(H_2O)_2^{2-}$
= $2[ZnS(HS)H_2O^-]$

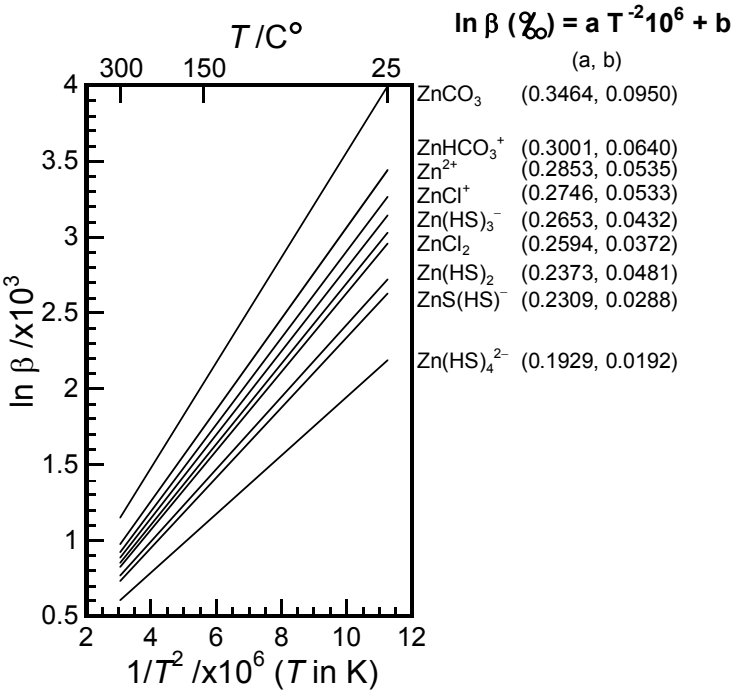


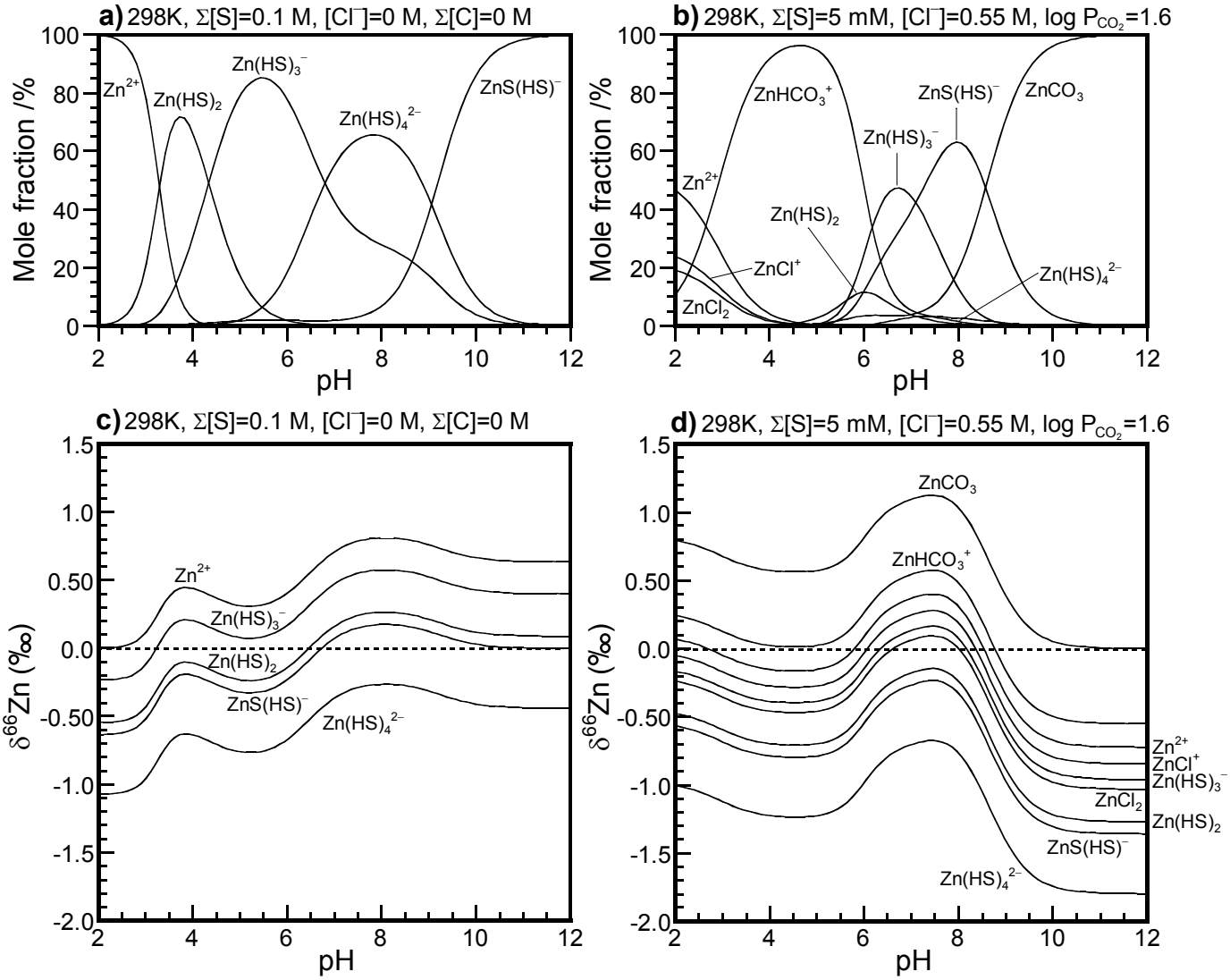
f) $ZnHCO_3(H_2O)_4^+$

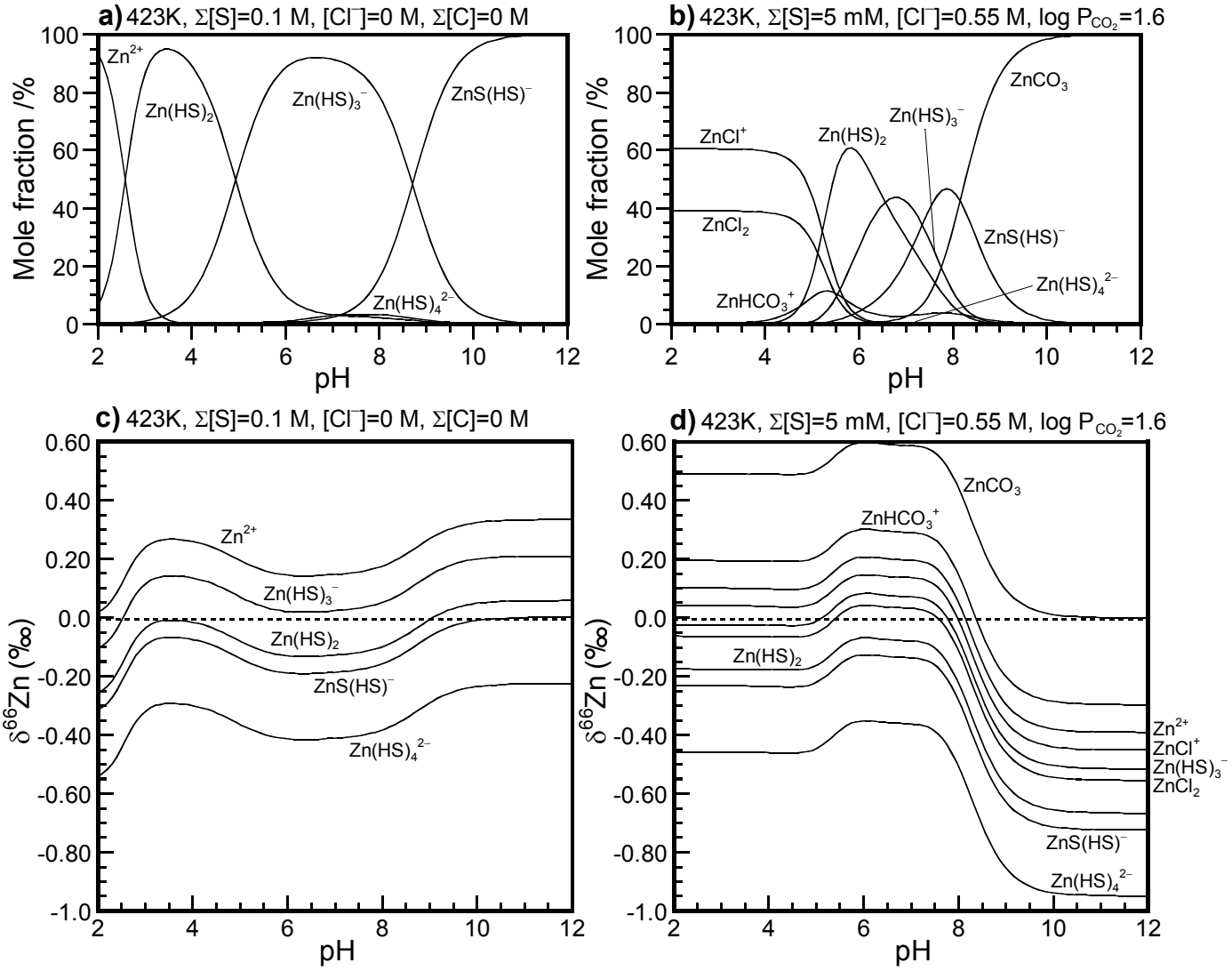


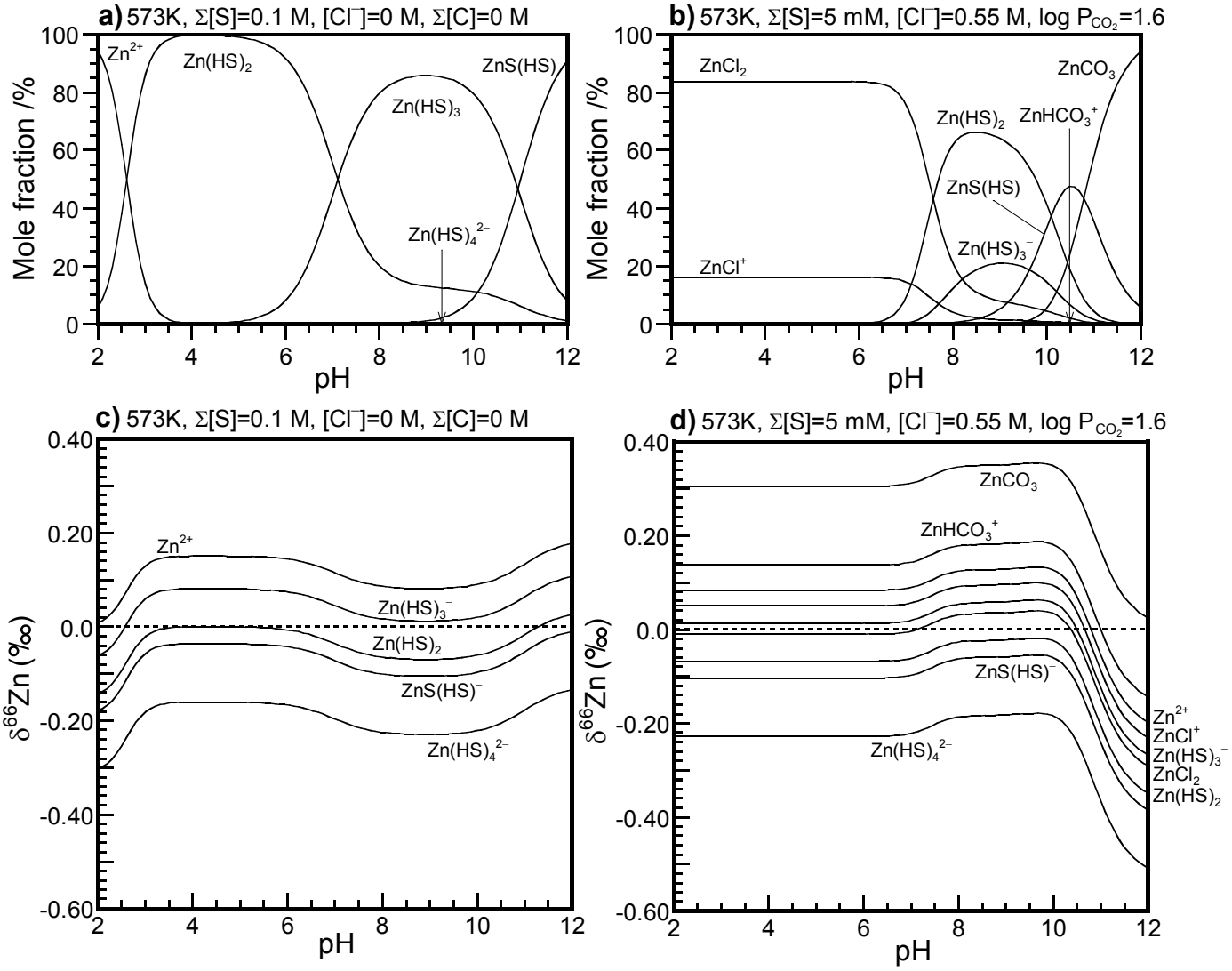
g) $ZnCO_3(H_2O)_4$











**Supplementary material**

# The origin of Zn Isotope Fractionation in Sulfides

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[3] Ecole Normale Supérieure de Lyon, Université de Lyon 1, CNRS, 46, Allee d'Italie, 69364 Lyon Cedex 7, France

In order of appearance:

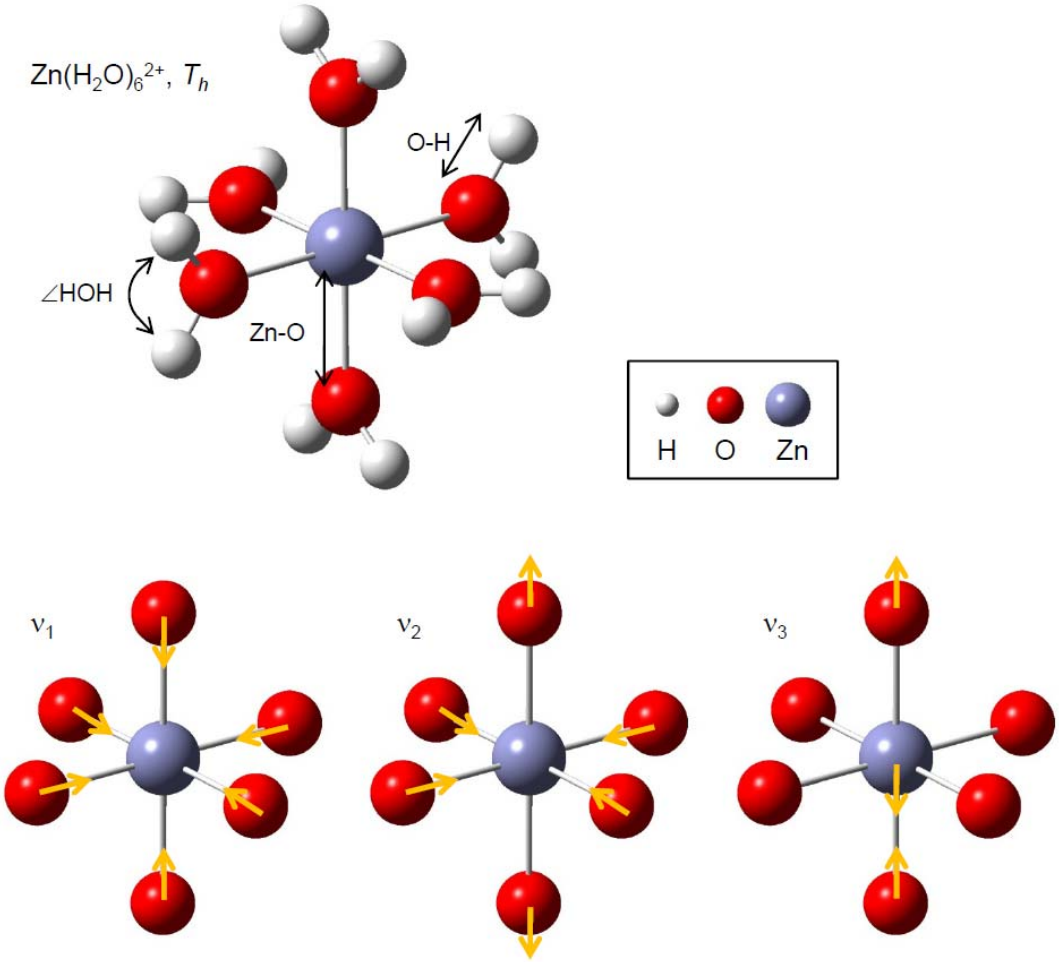


Fig. S1 $Zn(H_2O)_6^{2+}$ with $T_h$ symmetry and its vibrational modes, $\nu_1$, $\nu_2$, and $\nu_3$. Structures are drawn by using GaussView3.0 (Gaussian Inc.).

Table S1
Zn-O and O-H bond lengths and ∠HOH angles

| Theory/Basis sets[a] | Zn-O (Å) | O-H (Å) | ∠HOH (˚) |
|---|---|---|---|
| B3LYP | | | |
| 6-31G(d) | 2.094 | 0.973 | 107.2 |
| 6-31G(d,p) | 2.092 | 0.969 | 107.4 |
| 6-31+G(d) | 2.124 | 0.974 | 107.4 |
| 6-31+G(d,p) | 2.125 | 0.970 | 107.6 |
| 6-31++G(d,p) | 2.125 | 0.970 | 107.6 |
| 6-311G(d) | 2.095 | 0.965 | 108.4 |
| 6-311G(d,p) | 2.097 | 0.966 | 107.3 |
| 6-311+G(d) | 2.118 | 0.966 | 108.2 |
| 6-311+G(d,p) | 2.128 | 0.967 | 107.4 |
| 6-311++G(d,p) | 2.128 | 0.967 | 107.4 |
| LanL2DZ & 6-31G(d) | 2.131 | 0.973 | 107.1 |
| LanL2DZ & 6-31G(d,p) | 2.131 | 0.968 | 107.1 |
| LanL2DZ & 6-31+G(d) | 2.143 | 0.974 | 107.1 |
| LanL2DZ & 6-31+G(d,p) | 2.145 | 0.970 | 107.3 |
| LanL2DZ & 6-31++G(d,p) | 2.146 | 0.970 | 107.3 |
| LanL2DZ & 6-311G(d) | 2.131 | 0.965 | 108.3 |
| LanL2DZ & 6-311G(d,p) | 2.138 | 0.966 | 107.1 |
| LanL2DZ & 6-311+G(d) | 2.135 | 0.966 | 108.0 |
| LanL2DZ & 6-311+G(d,p) | 2.146 | 0.967 | 107.1 |
| LanL2DZ & 6-311++G(d,p) | 2.146 | 0.967 | 107.1 |
| UHF | | | |
| LanL2DZ & 6-31G(d) | 2.142 | 0.954 | 107.3 |

[a] Orbital geometries and vibrational frequencies of aqueous Zn(II) species were computed using density functional theory (DFT) as implemented by the Gaussian03 code (Frisch et al., 2003). The DFT method employed here is a hybrid density functional consisting of Becke's three-parameter non-local hybrid exchange potential (B3) (Becke, 1993) with Lee-Yang and Parr (LYP) (Lee et al., 1988) non-local functionals. 6-31G and 6-311G basis set, which are all-electron basis sets, were chosen for H, O, and Zn. For comparison, an effective-core potential (ECP) basis set, LanL2DZ (Hay and Wadt, 1985a, b; Wadt and Hay, 1985), was tested for Zn. Unrestricted Hartree-Fock (UHF) theory was also tested.

Table S2
$\nu_1$, $\nu_2$, and $\nu_3$ frequencies

| Theory/Basis sets | $\nu_1$ ($cm^{-1}$) | $\nu_2$ ($cm^{-1}$) | $\nu_3$ ($cm^{-1}$) |
|---|---|---|---|
| B3LYP | | | |
| 6-31G(d) | 361 | 236 | 295 |
| 6-31G(d,p) | 361 | 235 | 300 |
| 6-31+G(d) | 336 | 217 | 290 |
| 6-31+G(d,p) | 334 | 215 | 289 |
| 6-31++G(d,p) | 335 | 216 | 289 |
| 6-311G(d) | 372 | 246 | 339 |
| 6-311G(d,p) | 371 | 244 | 334 |
| 6-311+G(d) | 340 | 228 | 308 |
| 6-311+G(d,p) | 333 | 219 | 294 |
| 6-311++G(d,p) | 333 | 219 | 294 |
| LanL2DZ & 6-31G(d) | 338 | 243 | 301 |
| LanL2DZ & 6-31G(d,p) | 338 | 243 | 309 |
| LanL2DZ & 6-31+G(d) | 327 | 234 | 306 |
| LanL2DZ & 6-31+G(d,p) | 325 | 231 | 304 |
| LanL2DZ & 6-31++G(d,p) | 325 | 231 | 304 |
| LanL2DZ & 6-311G(d) | 342 | 250 | 329 |
| LanL2DZ & 6-311G(d,p) | 337 | 245 | 319 |
| LanL2DZ & 6-311+G(d) | 335 | 244 | 323 |
| LanL2DZ & 6-311+G(d,p) | 328 | 236 | 311 |
| LanL2DZ & 6-311++G(d,p) | 328 | 236 | 311 |
| UHF | | | |
| LanL2DZ & 6-31G(d) | 336 | 234 | 309 |

Table S3:
ln β's at 298 K

| Theory/Basis sets | ln β (‰) |
|---|---|
| B3LYP | |
| 6-31G(d) | 3.427 |
| 6-31G(d,p) | 3.405 |
| 6-31+G(d) | 3.274 |
| 6-31+G(d,p) | 3.215 |
| 6-31++G(d,p) | 3.214 |
| 6-311G(d) | 4.190 |
| 6-311G(d,p) | 4.044 |
| 6-311+G(d) | 3.501 |
| 6-311+G(d,p) | 3.250 |
| 6-311++G(d,p) | 3.239 |
| LanL2DZ & 6-31G(d) | 3.753 (3.74[a]) |
| LanL2DZ & 6-31G(d,p) | 3.732 |
| LanL2DZ & 6-31+G(d) | 3.520 |
| LanL2DZ & 6-31+G(d,p) | 3.465 |
| LanL2DZ & 6-31++G(d,p) | 3.474 |
| LanL2DZ & 6-311G(d) | 4.085 |
| LanL2DZ & 6-311G(d,p) | 3.838 |
| LanL2DZ & 6-311+G(d) | 3.859 |
| LanL2DZ & 6-311+G(d,p) | 3.600 |
| LanL2DZ & 6-311++G(d,p) | 3.598 |
| UHF | |
| LanL2DZ & 6-31G(d) | 3.594 (3.58[a]) |

[a] Black et al. (2011)

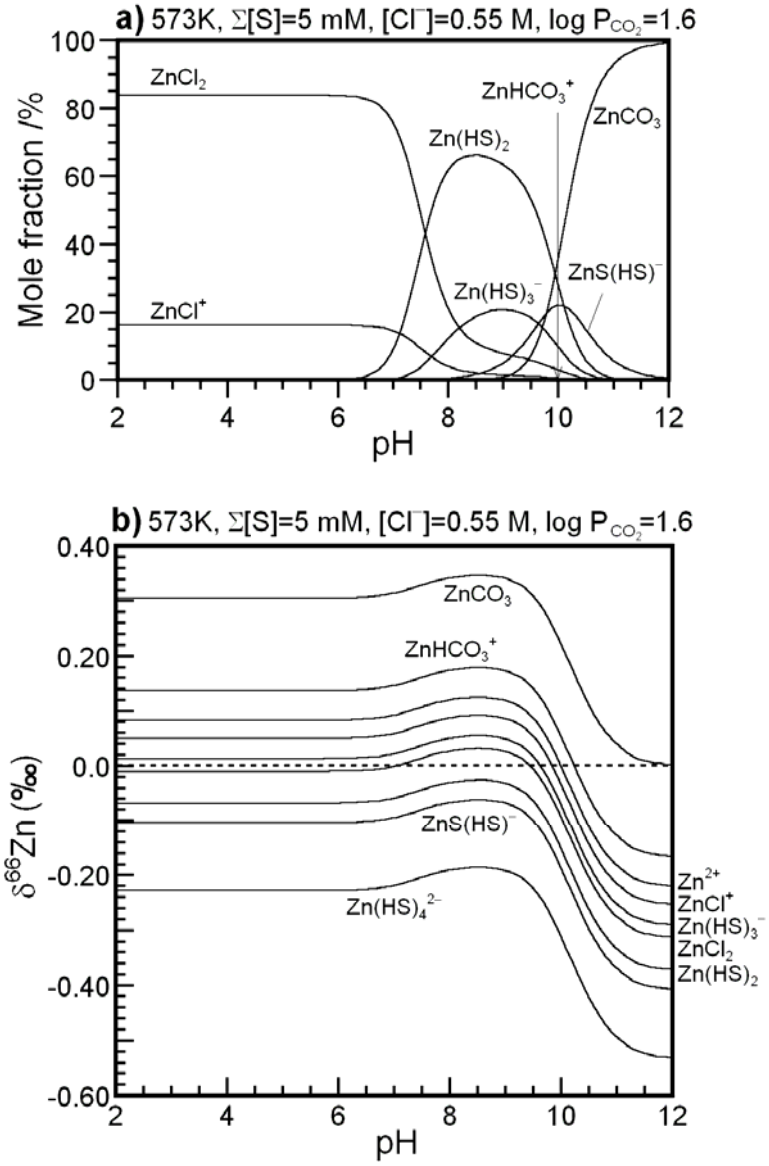


Fig. S2. Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K (for stronger complexation of Zn carbonates). a) Mole fractions of Zn species with Σ[S]=5 mM and [$Cl^-$] = 0.55 M under $P_{CO2}$ = 50 bar, b) $\delta^{66}$Zn under the hydrothermal condition. Under an assumption that formations of $ZnHCO_3^+$ and $ZnCO_3$ are enhanced by increasing temperature, $K_{ZnHCO_3^+}$ and $K_{ZnCO_3}$ were multiplied by 10 (as an example) and log $K_{ZnHCO_3^+}$ = 3.1 and log $K_{ZnCO_3}$ = 6.3 were used. Mole fraction of $Zn^{2+}$ in Fig. S2b is smaller than 0.001%. The maximum value of $Zn(HS)_4^{2-}$ mole fraction is 0.0002% at pH=9.3. The maximum value of $ZnHCO_3^+$ mole fraction is 0.5% at pH= 10.0. Dotted line in b) means $\delta^{66}$Zn of bulk solution (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn] was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

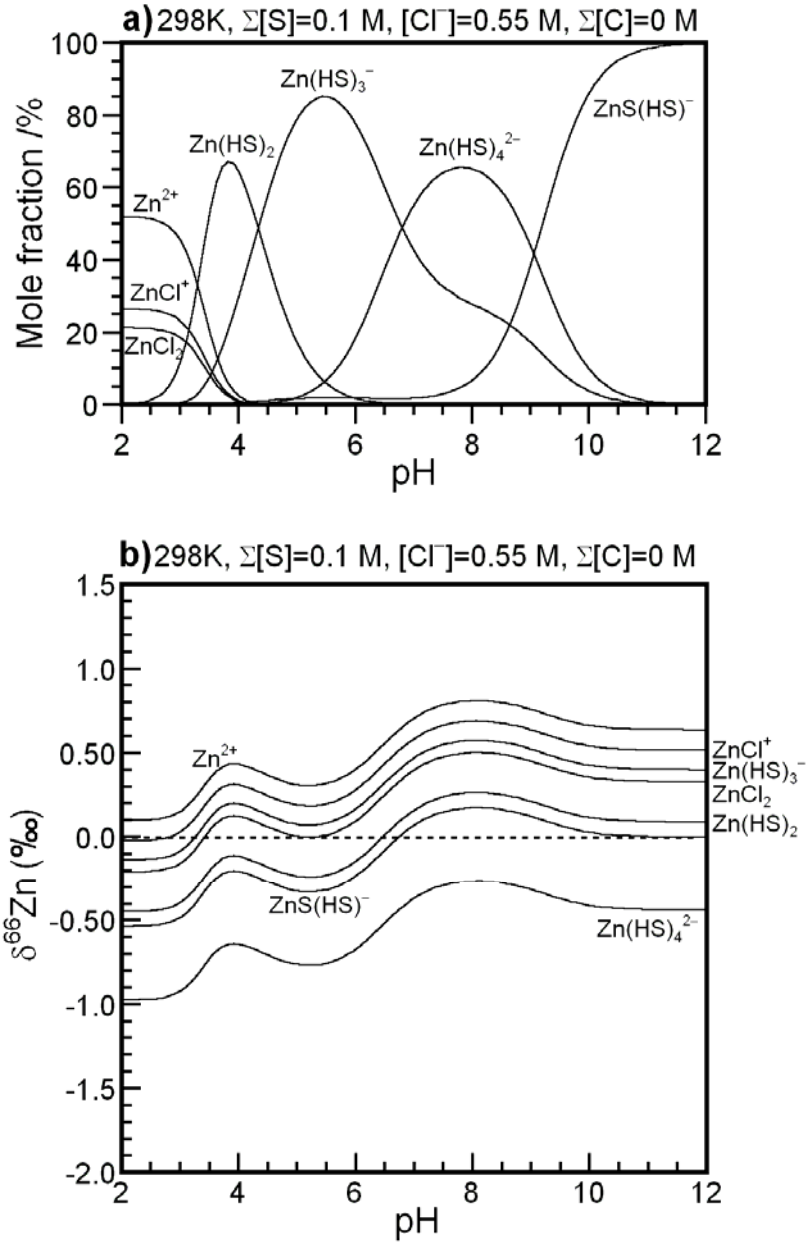


Fig. S3
Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K (Σ[S] = 0.1 M, [$Cl^-$] = 0.55 M, and Σ[C] = 0 M). a) Mole fractions of Zn species in carbonate free hydrous fluid under Σ[S]=0.1 M and [$Cl^-$] = 0.55 M, b) $\delta^{66}$Zn in carbonate free hydrous fluid. Dotted line in b) means $\delta^{66}$Zn of bulk solution (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn] was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

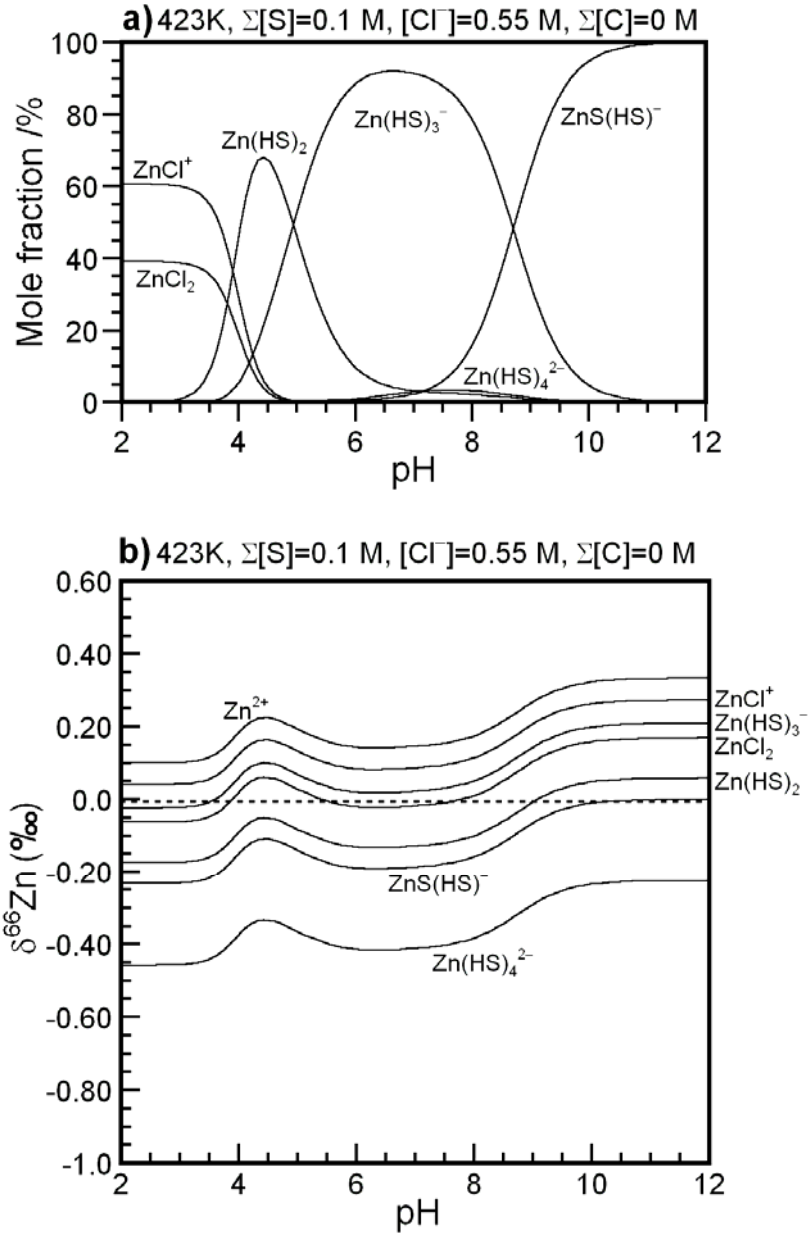


Fig. S4
Mole fractions of Zn species and Zn isotopic variations as functions of pH at 423 K (Σ[S] = 0.1 M, [$Cl^-$] = 0.55 M, and Σ[C] = 0 M). a) Mole fractions of Zn species in carbonate free hydrous fluid under Σ[S]=0.1 M and [$Cl^-$] = 0.55 M, b) $\delta^{66}$Zn in carbonate free hydrous fluid. Mole fraction of $Zn^{2+}$ is 0.14% at pH=2 and smaller than that at pH>2. Dotted line in b) means $\delta^{66}$Zn of bulk solution (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn] was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

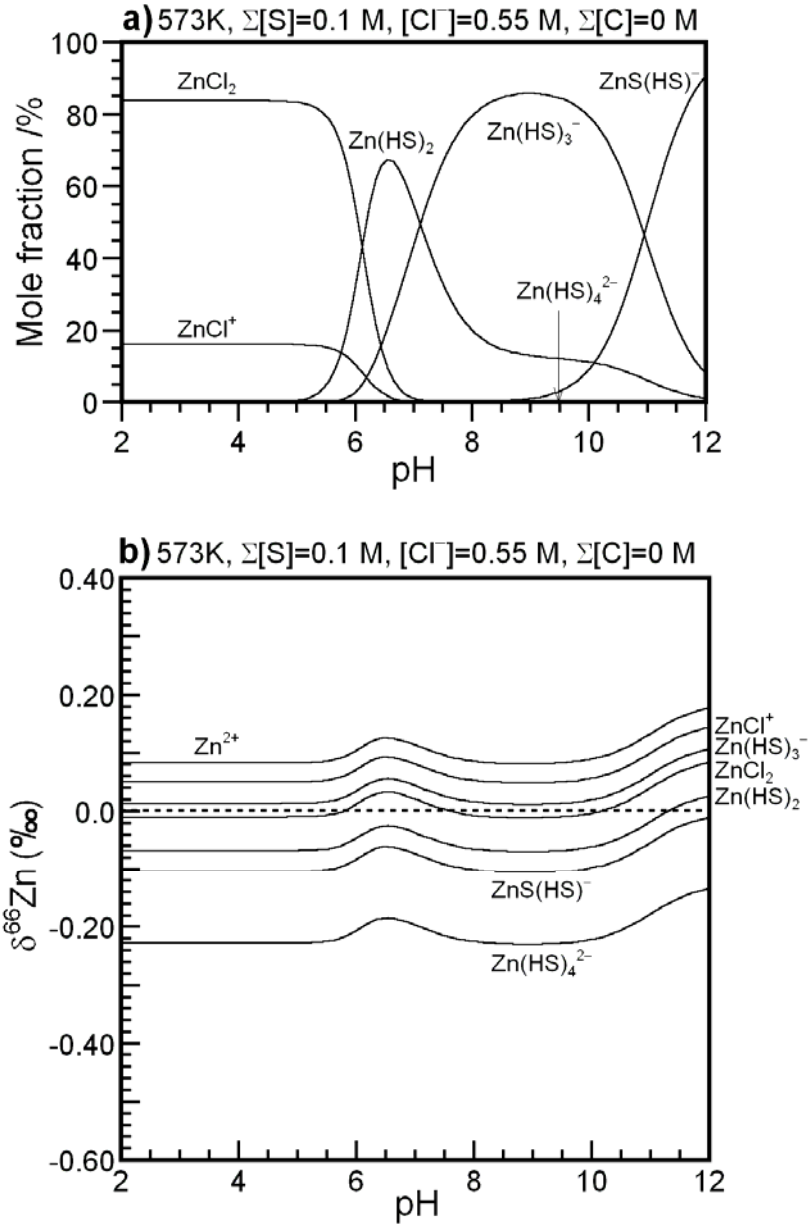


Fig. S5
Mole fractions of Zn species and Zn isotopic variations as functions of pH at 573 K (Σ[S] = 0.1 M, [$Cl^-$] = 0.55 M, and Σ[C] = 0 M). a) Mole fractions of Zn species in carbonate free hydrous fluid under Σ[S]=0.1 M and [$Cl^-$] = 0.55 M, b) $\delta^{66}$Zn in carbonate free hydrous fluid. Mole fraction of $Zn^{2+}$ is smaller than 0.001%. The maximum value of $Zn(HS)_4^{2-}$ mole fraction is 0.02% at pH=9.5. Dotted line in b) means $\delta^{66}$Zn of bulk solution (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn] was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

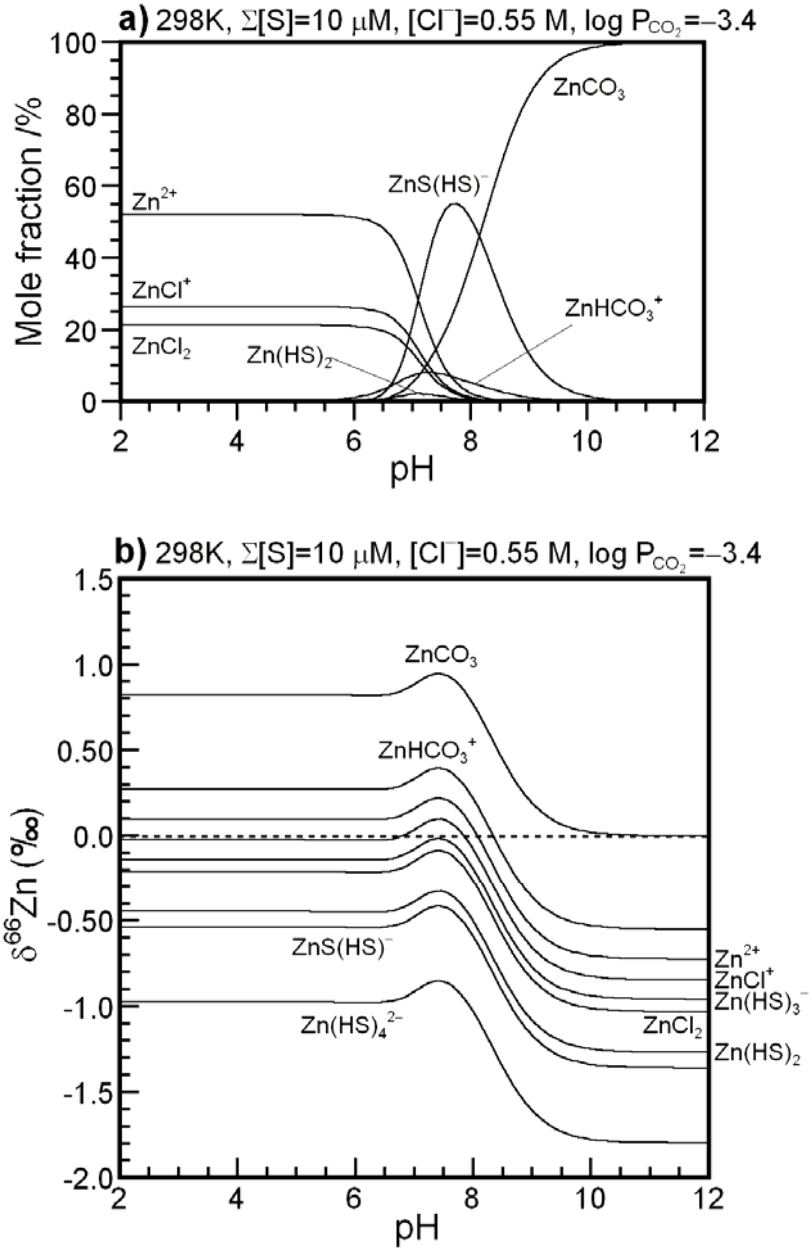


Fig. S6
Mole fractions of Zn species and Zn isotopic variations as functions of pH at 298 K (Σ[S] = 10 μM, [Cl$^-$] = 0.55 M, and log $P_{CO2}$ = –3.4). a) Mole fractions of Zn species in hydrous fluid under low Σ[S] and $P_{CO2}$ condition, b) $\delta^{66}$Zn in the hydrous fluid. Σ[S] and $P_{CO2}$ were set much smaller than those of Figs. 3a and 3c. The maximum value of $Zn(HS)_3^-$ mole fraction is 0.06% at pH=7.3. The maximum value of $Zn(HS)_4^{2-}$ mole fraction is 0.00001% at pH=7.4. Dotted line in b) means $\delta^{66}$Zn of bulk solution (averaged $\delta^{66}$Zn in the whole solution). Σ[Zn] was set to be $10^{-6.1}$ M (Tagirov and Seward, 2010).

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